

CHEMISTRY 3

EXPLANATORY AND SUPPLEMENTARY NOTES

To accompany the text-books used in the course:—HILL, *Lecture Notes on Qualitative Analysis*, and NOYES, *Detailed Course of Qualitative Chemical Analysis*

THIRD EDITION



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QUALITATIVE ANALYSIS.*

READING.

The following syllabus will indicate the nature of the reading which is required in this course :—

Reactions, meaning of.

Use of symbols and formulae.

Expression of a reaction by means of an equation.

The Gas Laws. Hypothesis of Avogadro.

Dissociation of molecules of a gas.

Present theories of solution.

Effect of dissolved substance on freezing and boiling point of solvent.

Osmotic Pressure. Hypothesis of Avogadro applied to solutions.

Conductivity of a solution. Electrolytes.

Electrolytic Dissociation. Ions.

Reactions regarded as taking place between ions. Expression of such reactions in the form of an equation.

Tests in qualitative analysis tests for ions.

Chemical Equilibrium. Balanced Actions.

Effect of Concentration (Law of Mass Action).

Measure of Concentration. Normal Solutions. Normality of a Solution.

Qualitative methods as influenced by the present theory of solution.

General directions in laboratory technique.

Reagents, precipitation, filtration, washing.

Reference books :—

Talbot and Blanchard, The Electrolytic Dissociation Theory.

Dobbin and Walker, Chemical Theory for Beginners.

Walker, Introduction to Physical Chemistry.

Jones, Theory of Electrolytic Dissociation.

Treadwell, Short Text-book of Analytical Chemistry: Part I, Qualitative Analysis.

Prescott and Johnson, Qualitative Chemical Analysis.

OUTLINE OF COURSE.

Systematic Qualitative Analysis, in the examination and identification of an unknown substance, comprehends the following steps :

- I. PRELIMINARY EXAMINATION in the dry way.
- II. SOLUTION of the substance.
- III. Analysis of the solution in the wet way for bases, or BASIC ANALYSIS.
- IV. Analysis of the solution in the wet way for acids, or ACID ANALYSIS.

For reasons that will be explained, instruction in these steps is not given in the above order, but the study of basic analysis precedes. Following this, the most common reactions in acid analysis are studied, after which the systematic examination of a large number of substances is taken up, in which the order of procedure follows that given above.

BASIC ANALYSIS.

Hill, pp. 1-14; 34-45; *Noyes*, pp. 15-49.

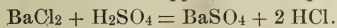
Before taking up the separation of the groups and detection of the bases, a preliminary study is made of the behavior of the bases toward certain reagents. (H., pp. 1-14.) Many of these reactions should be familiar through the study of general chemistry. Those which are of especial qualitative importance are indicated below and are to be carefully studied. Mark the corresponding paragraph in *Hill*. Take brief notes on the sheets provided for the purpose and write the equation for the reaction in its proper place.

This preliminary work on the properties of bases is to be performed, noted, and the note-sheets checked by one of the instructors before any solution for analysis will be given out.

Example of style of notes desired on the preliminary work:—

To chlorides of Ba, Sr, Ca added dil. H_2SO_4 .

(1) Ba. Immediate ppte, baric sulphate, white.



PRELIMINARY WORK ON THE PROPERTIES OF GROUPS I-II.

Group I. (H., pp. 2-3.)

Sources: Potassic nitrate and sodic chloride, dissolved in very little water; solutions of ammoniac chloride (reagent) and lithic chloride.*

Chlorplatينات. In watch glasses, to few drops of K, Na, Li, and H_4N solutions, add drop of chlorplatinic acid. Precipitate may be slow in forming. If so, add few drops alcohol (R).†

Flame Tests for K, Li, Na. In watch glasses place drop of concentrated solution and add drop dilute hydrochloric acid. Or, moisten very small crystal with drop hydrochloric acid. Ignite wire before using until it ceases to color flame. Observe also the color

* All solutions not included among the ordinary reagents will be found on the end desk.

† R means that the equation for the reaction is to be written.

of the flame through blue glass, which must be of sufficient thickness to cut out the yellow flame of the Na.

Spectroscope Tests. (H., p. 44.) Use same preparations as in flame tests. Note position of lines carefully.

Ammonium. Try test for NH_4 , according to H., p. 45; N., p. 49 (R).

Group II. (H., pp. 3-5.)

Sources : Solutions of chlorides of barium and calcium (reagents), strontium and magnesium.

Concentration and Volume of Solutions. The strength of solutions to be used in this work will depend somewhat upon the reaction to be studied. In general, however, a reaction can be more clearly observed when the concentration is not great; a few centigrams of substance dissolved in 10 c.c. of water will usually suffice. For such solutions as are given out for the study of reactions (end desks) the normality is marked on the bottle; this will be from N/200 to N/50. In preparing a solution from a laboratory reagent, however, it is best to begin with a normality of N/100; a stronger or weaker solution can be made if necessary. In every case the normality must be noted and a definite amount of solution taken, since it is important that the student should learn to estimate approximately the amount of substance present from the intensity of a given reaction in known concentration.

The amount of *solution* used should not exceed 10 c.c. Unless directions are given to the contrary, no more *reagent* should be added than is necessary to complete the reaction. Hence the reagent is to be added drop by drop to the occasionally shaken test tube until it is evident that no further change takes place. The approximate amount of reagent needed can be estimated, of course, from the normality of the reagent.

The normality of the common reagents may be found from the list on page 56.

Hydroxides. Try ammonic hydroxide on solutions of Ba, Sr, Ca, and Mg (R).

Add ammonic chloride to precipitate if formed (R).

Carbonates. Try sodic carbonate on Ba (R), Sr, Ca, Mg (R).

Try ammoniac carbonate on Ba (R), Sr, Ca, Mg (R). Try to dissolve in ammoniac chloride.

Sulphates. Try dilute sulphuric acid on Ba (R), Sr (R), Ca, diluted and undiluted (R), Mg, diluted and undiluted.

Precipitate Ca, undiluted, with magnesian sulphate (R); Sr, undiluted, with calcic sulphate (R); Ba with strontic sulphate (R).

(To make solution of strontic sulphate, precipitate the sulphate hot, allow to settle, pour off, and wash the precipitate repeatedly with hot water until washwater gives no test for sulphate with baric chloride. Then add considerable water and allow to stand over night.)

Chromates. Try (Ba) R, Sr, Ca, Mg with potassic chromate. Divide baric chromate precipitate into two parts; to one add hydrochloric acid (R), to the other acetic.

Phosphates. Try Ba (R), Sr, Ca, Mg (R) with sodic phosphate. Dissolve in a few drops of hydrochloric acid (R). Re-precipitate with ammoniac hydroxide (R).

Oxalates. Try Ba, Sr, Ca (R), Mg with ammoniac oxalate. Divide the calcic oxalate into two parts; to one add hydrochloric acid (R), to the other acetic.

Flame and Spectroscope Tests for Ba, Sr, Ca. (H., p. 44.) To the solution in watch glass add dilute hydrochloric acid and test as under Group I. Note position of lines.

ANALYSIS OF KNOWN AND UNKNOWN SOLUTIONS, GROUPS I-II.

Known Solution.

After the preliminary work on Groups I-II, a known solution, containing Ba, Sr, Ca, Mg, K, Na, Li, H_4N , is to be analyzed according to H., pp. 42-45. Any deviations from the method given in *Hill* will be found under the head of "Additions and Corrections, Basic Analysis," p. 22, below. The method given in *Noyes*, pp. 44-49, must also be studied.

Notes (on sheets provided for the purpose) are to be taken on the analysis of the known solution according to the general plan suggested below for the unknown solutions, but should be written out with more detail than is expected on the unknown solutions. The equations for the most important separations and tests, as called for under "Equations for Reactions," p. 19, below, are to be written in their proper place as part of the notes on the known solution.

Studies of Reaction Limits.

After the known solution, a study is made of typical reactions, in order to find out approximately in what concentration and under what conditions the presence of an ion may be recognized.

Rough Graduation of Test-Tube. Heat a small part of the rim of a dry test-tube until soft, then with a warm file press the rim slightly outward to make a lip. Rinse the test-tube with water and allow it to drain. Graduate it as follows: Let the water run out of a measuring burette until the lower meniscus of the water is at any whole division. Allow 3 c.c. of the water to run into the test-tube. Holding the tube upright, mark with sharp file at lower meniscus. Pour out the water, allow it to drain. Add 10 c.c. water and mark. Repeat with two more portions of 10 c.c.

With these graduations of 3, 10, 20, and 30 c.c., one can roughly dilute a given volume two, three or ten-fold.

A. The Test for Magnesium. Dilute 3 c.c. magnesium sulphate (N/1) to 30 c.c. Call this Solution II. How many milligrams of magnesium per c.c. does this contain?

To 10 c.c. Solution II add about 1 c.c. ammoniac chloride, then about 1 c.c. ammoniac hydroxide, and finally about 1 c.c. sodic phosphate. Set aside.

Dilute 3 c.c. of Solution II to 30 c.c. (Solution III). Precipitate this solution as above, but using only a few drops of each reagent. Set aside.

Dilute 3 c.c. of Solution III to 30 c.c. (Solution IV). Add reagents as above. If no immediate precipitate, note time and set aside. If precipitate forms on standing, note time taken for formation.

What amount of magnesium does the 10 c.c. of Solution IV represent? Can the test be further extended? How? Suppose, in

Solution IV, no precipitate results on standing, how would one then find the limit of the reaction under the conditions?

B. The Precipitation of Barium Chromate in Acetic Acid Solution. Dilute 3 c.c. baric chloride solution (N/1) to 30 c.c. (Solution II). To 10 c.c. of this solution add a few drops of ammoniac hydroxide, then acetic acid in slight excess, then about 1 c.c. potassic chromate. Set aside.

Dilute Solution II to ten times its volume (Solution III) and test a part as above, using, however, only a few drops of potassic chromate.

Dilute Solution III to ten times its volume (Solution IV) and test as above.

From the method indicated by this experiment and the preceding, calculate the concentration from which barium may be precipitated under these conditions.

Try Solution IV with potassic chromate, but without adding ammoniac hydroxide and acetic acid. Is there any difference in result? Can a reason be assigned for such difference?

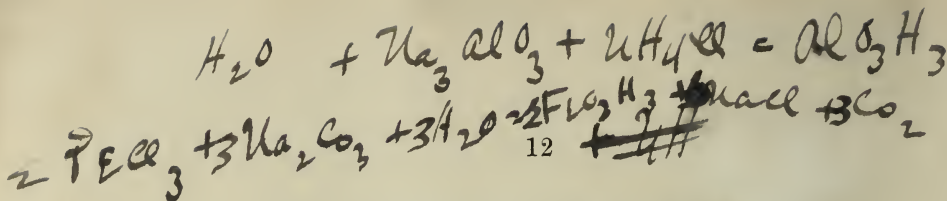
Record Experiments *A* and *B* on sheets provided for the purpose.

Unknown Solutions.

After Experiments *A* and *B*, two unknown solutions are to be analyzed. To obtain these, hand in bottles (125 c.c.) labelled with desk number and serial number of analysis, thus: $\frac{99}{1}$. These solutions contain one or more of the members of Groups I-II, and are to be analyzed like the known solution, except where the evident absence of a portion of the group makes an examination for that portion unnecessary.

Notes on the unknown solutions, which are to be recorded in the Analysis Notebook, should be concise, — simply stating results and conclusions in the briefest form consistent with accuracy. Begin each solution on a fresh page. An example is given in the following:—

08.72 in liter 10000
 .006872
 .0206872
 12.18 in 81.21
 .00117100



GENERAL PLAN OF NOTES ON THE UNKNOWN SOLUTIONS.

Unknown Sol. No. 1

Oct. 10, 1900

Mixed sol. with lime

Turmeric faintly brown

∴ NH₄, tr

To sol. added H₄NCl, H₄NOH, (H₄N)₂CO₃

Heavy ppte.

Filt., washed, dissolved in HC₂H₃O₂

To part added CaSO₄

No ppte. on long standing

To rest added H₄NOH, (H₄N)₂C₂O₄

Heavy white ppte.

∴ Ca

Filtrate from carbonates:

To part added Na₂HPO₄

White ppte.

∴ Mg

Evaporated rest of sol., ignited, removed Mg by Ba(OH)₂, removed Ba by H₂SO₄ and ignited.

No residue.

Solution contains magnesium, considerable calcium and traces of ammonium.

PRELIMINARY WORK ON THE PROPERTIES OF GROUPS III-IV.

Group III. (H., pp. 5-6.)

Sources: Solutions of nitrates or sulphates of aluminum and chromium; see paragraph, *Concentration and Volume of Solutions*, page 8.

Hydroxides. Add cautiously sodic hydroxide to both Al and Cr solutions until the precipitate dissolves (R). Boil both solutions (R). To the sodic aluminate add ammonic chloride (R). If no precipitate, heat.

Precipitate aluminic and chromic hydroxides with ammonic hydroxide (R). What is the effect of heat, before or after precipitation?

Oxides. Filter off the hydroxides, dry them over hot plate, and fuse on platinum foil with about two parts sodic carbonate and one part potassic nitrate. The fusion should be quite liquid, and gas effervescence should cease (R). Boil the fusion with water, filter if necessary, and test the filtrates, — for Al with ammonic chloride (R), for Cr with acetic acid and plumbous acetate (R). In the latter

case be sure that acetic acid is in excess. Yellow precipitate of plumbous chromate shows presence of chromate.

To Cr solution add sodic hydroxide in excess and heat to boiling. Add, in very small quantities at a time, solid sodic peroxide until the precipitate of chromic hydroxide disappears and the solution is a clear yellow (R). Boil off excess of oxygen and test for chromate as above.

Sulphides. Not formed. Precipitate the hydroxides with ammoniac sulphide (R).

Carbonates. Not formed. Precipitate the hydroxides with ammoniac carbonate (R).

Group IV. (H., pp. 6-9.)

Sources: Solutions of nitrates of zinc, manganese, nickel and cobalt; ferric chloride (reagent); ferrous sulphate, reduced before using with card teeth and a few drops of sulphuric acid; see paragraph, *Concentration and Volume of Solutions*, page 8.

Hydroxides. Add sodic hydroxide to all, cautiously (R*). Heat the tube containing the cobaltous hydroxide and notice change of color. Dissolve all in a *little* dilute hydrochloric acid (R), and re-precipitate with sodic hydroxide.

Notice oxidation of ferrous and manganous hydroxides in air (R). To a portion of these add bromine water, and observe oxidation (R). To rest of hydroxides add bromine water (R).

Precipitate zincic hydroxide with sodic hydroxide (R), then add excess (R). Boil with ammoniac chloride. Compare aluminum.

Precipitate the hydroxides with ammoniac hydroxide (R), then add excess. Note carefully the solvent effect of excess.

To the several solutions add considerable ammoniac chloride, then ammoniac hydroxide. What hydroxides are precipitated and to what extent? What conclusion can you draw, from *your* work, as to separation of Al, Cr, and Fe^{III} from the others by means of ammoniac hydroxide in presence of ammoniac chloride?

Sulphides. To the solutions add a few drops of dilute hydrochloric acid, then hydrogen sulphide in excess. To what is the precipitation in the ferric solution (R) due?

* Equations involving merely a difference in base need not be written in this or future cases.

Now add ammoniac hydroxide (why ~~is~~ this equivalent to adding ammoniac sulphide?), then ammoniac sulphide in excess. The product of hydrogen sulphide on the ferric solution should be divided into two parts, for comparison, before precipitating.

Now add considerable dilute hydrochloric acid, and note difference in solvent effect (R).

Neutralize fresh zinc solution with sodic hydroxide, then acidify with acetic acid and precipitate with hydrogen sulphide (R).

Carbonates. To all add sodic carbonate (R). What is precipitated from the ferric solution? Compare Al and Cr.

ANALYSIS OF KNOWN AND UNKNOWN SOLUTIONS, GROUPS III-IV.

Known Solution.

After the preliminary work on Groups III and IV, the known solution containing these groups is to be analyzed according to H., pp. 38-42, with reference to the "Additions and Corrections," and to N., pp. 29-44. Notes and equations for reactions are also to be written, as explained under Groups I-II.

Studies of Reaction Limits.

After the known solution, the following experiments are to be performed and recorded on sheets.

C. Precipitation of Zinc as Sulphide. Dilute 3 c.c. zinc solution to N/100. To 10 c.c. of this solution add a few drops of ammoniac hydroxide until the precipitate redissolves, acetic acid in slight excess, then hydrogen sulphide. Set aside. Note nature of precipitate.

Dilute a portion of the N/100 solution to N/1000, and test as above.

In what concentration is zinc recognizable under these conditions?

D. Oxidation of Nickel in Alkaline Cyanide Solution. Take 10 c.c. of a N/100 solution of nickel. Precipitate by sodic hydroxide, filter, wash, dissolve in very small amount of potassic cyanide, add

excess of sodic hydroxide, then bromine in excess. Note nature and amount of precipitate.

Repeat with 10 c.c. of a N/1000 solution. If no precipitate at once, look for dark color and slight precipitate on standing.

In what concentration are you able to recognize the presence of nickel by this test?

E. Thiocyanate Test for Iron. To a given volume of N/10 ferric solution add potassic thiocyanate; also to a N/100 solution. Dilute further and test. Continue until you find the limit of concentration in which the presence of iron may be recognized by this test.

Unknown Solutions.

Two unknown solutions containing one or more of the members of Groups I-IV are now to be analyzed, and recorded in the Analysis Notebook.

PRELIMINARY WORK ON THE PROPERTIES OF GROUP V.

Group V. (II., pp. 9-12.)

Sources: Solutions of cupric, cadmic and bismuthous nitrates. The other solutions (reagents) are: argentic nitrate, mercurous nitrate, mercuric chloride, plumbous acetate; see paragraph, *Concentration and Volume of Solutions*, page 8.

Oxides and Hydroxides. Precipitate all with sodic hydroxide, cautiously (R), then add excess (R). Boil the precipitate of cupric hydroxide.

Add ammoniac hydroxide to fresh portions of all, cautiously, then excess.

Fehling's Test. To equal volumes of cupric sulphate solution and alkaline tartrate (the mixture should be a clear blue) add a bit of glucose or few drops of glucose solution. Boil (R).

Sulphides. Add hydrogen sulphide to all, in excess (R). Add dilute nitric acid; boil if solution does not take place at once (R).

Repeat precipitation of sulphides in solution containing about one-fourth volume of concentrated hydrochloric acid. For this test, the solutions of silver, mercurous, and lead need not be used. What effect on the precipitation does the acid have?

Chlorides. Precipitate silver, lead, and mercurous by dilute hydrochloric acid (R). Warm the precipitate of plumbous chloride until dissolved. Cool. Filter the cold precipitated plumbous chloride and test for lead in filtrate with sulphuric acid or hydrogen sulphide.

Add ammoniac hydroxide to the precipitated chlorides (R).

Boil down the solution of bismuthous nitrate nearly to dryness, and add the residue, which must contain little or no free acid, to water (R). If no precipitate, add few drops ammoniac chloride.

ANALYSIS OF KNOWN AND UNKNOWN SOLUTIONS, GROUP V.

Known Solution.

After the preliminary work on Group V, the known solution containing this group is to be analyzed according to H., pp. 35-37; with reference to the "Additions and Corrections," and to N., pp. 16-23. Notes and equations for reactions are also to be written.

Studies of Reaction Limits.

F. Ammonia Test for Copper. Dilute a N/10 solution of copper to N/100. To a given volume of this add slight excess of ammoniac hydroxide. Set aside; observe color.

Dilute further and test. Continue until you find the limit of concentration at which copper is recognizable by this test.

G. Precipitation of Lead as Sulphate. Make a N/10 solution of lead. Add a few drops of dilute sulphuric acid. Set aside. Observe precipitate.

Make a N/1000 solution, and test as before. Try also a N/1000 solution. If no precipitate, evaporate almost to dryness (until fumes of sulphuric acid appear), cool, add water, transfer to test tube and allow to stand. Note if sediment settles, which, on twirling the tube, may be seen to rise in a spiral form.

In what concentration can you recognize lead by this method?

Unknown Solutions.

Two unknown solutions, containing one or more members of Group V, are now to be analyzed, and recorded in the Analysis Notebook.

PRELIMINARY WORK ON THE PROPERTIES OF GROUP VI.

Group VI. (H., pp. 13-14.)

Sources : Neutral solutions of sodic arsenite and sodic arseniate ; acid solutions of antimonious chloride, stannous and stannic chlorides ; see paragraph, *Concentration and Volume of Solutions*, page 8.

Hydroxides. To antimonious chloride, stannous and stannic chlorides, add a few drops more sodic hydroxide than is sufficient to neutralize free acids (R), then excess (R).

Sulphides. To sodic arsenite (a) and sodic arseniate (b) add hydrogen sulphide. Why no precipitate? To (a) add slight excess dilute hydrochloric acid (R), filter, and wash the precipitate free from acid. To (b) add acid. Why no precipitate at once? Add more hydrogen sulphide, cork tube, and allow to stand over night (R). To another portion of (b) add concentrated hydrochloric acid, heat to boiling and add excess of hydrogen sulphide. Keep hot, adding more hydrogen sulphide if necessary, until precipitate forms (R).

Precipitate Sb (R), Sn^{II} (R), and Sn^{IV} (R) with hydrogen sulphide, best in warm solution, filter when settled, and wash free from acid.

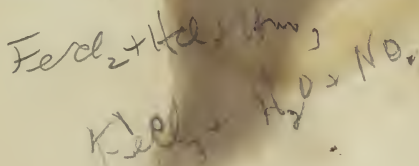
Transfer to tube with about 10 c.c. water the washed sulphides of As, Sb, Sn^{II} and Sn^{IV} . Add 5 c.c. ammoniac sulphide, and warm gently if necessary. Stannous sulphide will not dissolve ; the others should (R). To the stannous sulphide add yellow ammoniac sulphide, drop by drop, until after digestion solution takes place (R).

To the sulpho-salts add dilute hydrochloric acid in excess (R).

To the two ammoniac sulphides add dilute hydrochloric acid (R).

ANALYSIS OF KNOWN SOLUTION, GROUPS V-VI.

After the preliminary work on Group VI, a known solution containing this group and bismuth is to be analyzed according to H., pp. 35-38, with reference to the "Additions and Corrections," and to N., pp. 16-26. Notes and equations for reactions are also to be written.



*PROBLEMS IN BASIC ANALYSIS; UNKNOWN SOLUTIONS,
GROUPS I-VI.*

After the above study of the groups, the analysis of a series of at least ten solutions is taken up, each containing one or more bases in Groups I-VI. This constitutes the main work of the first half-year.

In analyzing these solutions, regard should always be paid to the possibility of shortening the general method in the absence of single bases or sub-groups. Brief but accurate notes are to be taken in the Analysis Notebook on each analysis, and the results summarized in the form of a report. No report will be accepted unless accompanied by sufficient notes to show how the analysis was made. On the other hand, voluminous notes are not desired.

EQUATIONS FOR REACTIONS.

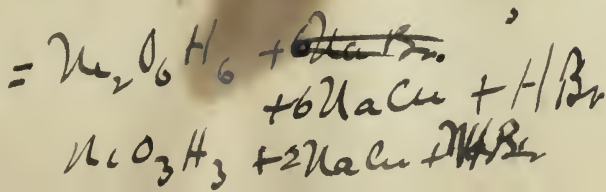
The following equations for reactions are to be written in their proper place in the notes on the analysis of the known solutions:—

Groups I, II.

1. Precipitation of carbonates: $M''Cl_2 + (H_4N)_2CO_3$.
2. Test for magnesium: $MgCl_2NH_4Cl + Na_2HPO_4 + H_4NOH$.
3. Solution of carbonates in acetic acid: $M''CO_3 + H(C_2H_3O_2)$.
4. Test for barium or strontium: $M''(C_2H_3O_2)_2 + CaSO_4$.
5. Elimination of barium: $Ba(C_2H_3O_2)_2 + K_2CrO_4$.
6. Re-precipitation of strontium and calcium: $M''CrO_4 + (H_4N)_2CO_3$.
7. Elimination of strontium: $Sr(C_2H_3O_2)_2 + H_2SO_4$.
8. Test for calcium: $CaSO_4 + (H_4N)_2C_2O_4$.
9. Elimination of magnesium: $MgCl_2 + Ba(OH)_2$.
10. Elimination of barium: $BaCl_2 + Ba(OH)_2 + H_2SO_4$.
11. Test for ammonium: $H_4NCl + Ca(OH)_2$.
12. Test for potassium: $KCl + H_2PtCl_6$.

Groups III, IV.

1. Reduction of ferric iron: $FeCl_3 + (H_4N)_2S$.
2. Precipitation of Fe, Co, Ni, Mn, Zn, as sulphides: $FeCl_2 + (H_4N)_2S$.
3. Precipitation of Al, Cr, as hydroxides: $AlCl_3 + (H_4N)_2S + H_2O$.
4. Solution of Fe, Mn, Zn sulphides in cold dilute hydrochloric acid: $FeS + HCl$.
5. Solution of Al, Cr hydroxides in cold dilute hydrochloric acid: $Al(OH)_3 + HCl$.
6. Solution of Co, Ni sulphides in aqua regia: $CoS + Cl_2$.
7. Test for Co: $CoCl_2 + H_4NCNS$.
8. Formation of potassic cobaltocyanide: $Co(OH)_2 + KCN$.
9. Formation of double cyanide of Ni and K: $Ni(OH)_2 + KCN$.
10. Test for Ni: $Ni(CN)_2 + NaOH + Br_2$.
11. Oxidation of potassic cobaltocyanide: $K_4Co(CN)_6 + Br_2$.
12. Oxidation of ferrous iron: $FeCl_2 + HCl + HNO_3$.
13. Partial neutralization by sodic carbonate: $Na_2CO_3 + HCl$.



14. Precipitation of Fe, Al, Cr, by baric carbonate: $\text{FeCl}_3 + \text{BaCO}_3 + \text{H}_2\text{O}$.
15. Solution of Fe, Al, Cr hydroxides in hydrochloric acid: $\text{Fe}(\text{OH})_3 + \text{HCl}$.
16. Solution of excess baric carbonate in hydrochloric acid: $\text{BaCO}_3 + \text{HCl}$.
17. Re-precipitation of Fe, Al, Cr hydroxides by ammonic hydroxide: $\text{FeCl}_3 + \text{H}_4\text{NOH}$.
18. Oxidation of chromic hydroxide to sodic chromate: $\text{Cr}(\text{OH})_3 + \text{Na}_2\text{O}_2$.
19. Formation of sodic aluminate: $\text{Al}(\text{OH})_3 + \text{NaOH}$.
20. Test for Cr: $\text{Na}_2\text{CrO}_4 + \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$.
21. Test for Al: $\text{Na}_3\text{AlO}_3 + \text{H}_4\text{NCl}$.
22. Removal of barium from Mn, Zn: $\text{BaCl}_2 + \text{H}_2\text{SO}_4$.
23. Precipitation of Mn: $\text{MnSO}_4 + \text{NaOH}$.
24. Solution of Zn as zincate: $\text{Zn}(\text{OH})_2 + \text{NaOH}$.
25. Formation of zincic acetate: $\text{Na}_2\text{ZnO}_2 + \text{H}(\text{C}_2\text{H}_3\text{O}_2)$.
26. Test for Zn: $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{H}_2\text{S}$.
27. Confirmatory test for Mn: $\text{MnO} + \text{K}_2\text{O} + \text{O}$.
28. Test for Fe'' : $\text{FeSO}_4 + \text{K}_3\text{Fe}(\text{CN})_6$.
29. Test for Fe''' : $\text{FeCl}_3 + \text{K}_4\text{Fe}(\text{CN})_6$.
30. Test for Fe''' : $\text{FeCl}_3 + \text{KCNS}$.

Group V.

1. Precipitation of silver: $\text{AgNO}_3 + \text{HCl}$.
2. Precipitation of lead: $\text{Pb}(\text{NO}_3)_2 + \text{HCl}$.
3. Precipitation of mercurous: $\text{Hg}_2(\text{NO}_3)_2 + \text{HCl}$.
4. Test for lead: $\text{PbCl}_2 + \text{H}_2\text{SO}_4$.
5. Test for mercurous: $\text{Hg}_2\text{Cl}_2 + \text{H}_3\text{N}$.
6. Solution of argentic chloride: $\text{AgCl} + \text{H}_3\text{N}$.
7. Detection of silver: $\text{AgClNH}_3 + \text{HNO}_3$.
8. Precipitation of group: $\text{M}''(\text{NO}_3)_2 + \text{H}_2\text{S}$.
9. Precipitation of group: $\text{Bi}(\text{NO}_3)_3 + \text{H}_2\text{S}$.
10. Solution of sulphides in nitric acid: $\text{PbS} + \text{HNO}_3$.
11. Solution of mercuric sulphide: $\text{HgS} + \text{Cl}_2$.
12. Precipitation of mercury by copper: $\text{HgCl}_2 + \text{Cu}$.
13. Test for mercury with stannous chloride: $\text{HgCl}_2 + \text{SnCl}_2$.
14. Test for and removal of lead: $\text{Pb}(\text{NO}_3)_2 + \text{H}_2\text{SO}_4$.

15. Precipitation of bismuth : $\text{Bi}_2(\text{SO}_4)_3 + \text{H}_4\text{NOH}$.
16. Test for copper : $\text{CuSO}_4 + \text{H}_4\text{NOH}$.
17. Test for copper : $\text{CuCl}_2 + \text{K}_4\text{Fe}(\text{CN})_6$.
18. Test for bismuth : $\text{Bi}(\text{OH})_3 + \text{HCl}$; $\text{BiCl}_3 + \text{H}_2\text{O}$.
19. Test for bismuth : $\text{SnCl}_2 + \text{NaOH}$; $\text{BiCl}_3 + \text{NaOH}$; $\text{Bi}(\text{OH})_3$
+ K_2SnO_2 .
20. Separation of copper from cadmium : $\text{CdS} + \text{H}_2\text{SO}_4$.
21. Test for cadmium : $\text{CdSO}_4 + \text{H}_2\text{S}$.

Group VI.

1. Precipitation of Bi, As, Sb : $\text{M}^{\text{III}}\text{Cl}_3 + \text{H}_2\text{S}$.
2. Precipitation of stannousum : $\text{SnCl}_2 + \text{H}_2\text{S}$.
3. Precipitation of stannicium : $\text{SnCl}_4 + \text{H}_2\text{S}$.
4. Solution of sulphides of As and Sb : $\text{As}_2\text{S}_3 + (\text{H}_4\text{N})_2\text{S}$.
5. Solution of stannous sulphide : $\text{SnS} + (\text{H}_4\text{N})_2\text{S} + \text{S}$.
6. Solution of stannic sulphide : $\text{SnS}_2 + (\text{H}_4\text{N})_2\text{S}$.
7. Re-precipitation of As and Sb : $(\text{H}_4\text{N})_3\text{AsS}_3 + \text{HCl}$.
8. Re-precipitation of Sn : $(\text{H}_4\text{N})_2\text{SnS}_3 + \text{HCl}$.
9. Solution of arsenious sulphide : $\text{As}_2\text{S}_3 + (\text{H}_4\text{N})_2\text{CO}_3$.
10. Re-precipitation of arsenious sulphide : $(\text{H}_4\text{N})_3\text{AsO}_3 +$
 $(\text{H}_4\text{N})_3\text{AsS}_3 + \text{HCl}$.
11. Test for arsenic : $\text{As}_2\text{S}_3 + \text{Na}_2\text{CO}_3 + \text{C}$.
12. Solution of antimonious sulphide : $\text{Sb}_2\text{S}_3 + \text{HCl} + \text{Cl}_2$.
13. Solution of stannic sulphide : $\text{SnS}_2 + \text{HCl} + \text{Cl}_2$.
14. Reduction of stannic chloride by iron : $\text{SnCl}_4 + \text{Fe}$.
15. Test for tin : $\text{SnCl}_2 + \text{HgCl}_2$.
16. Precipitation of antimony by iron : $\text{SbCl}_5 + \text{Fe}$.
17. Confirmation of Sb : $\text{Sb} + \text{Cl}_2$; $\text{SbCl}_5 + \text{H}_2\text{S}$.

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*ADDITIONS AND CORRECTIONS IN THE GENERAL METHOD
OF BASIC ANALYSIS.*

Groups V-VI.

It is evident that the number of bases ordinarily to be looked for in a solution is not large, and that all the groups are not necessarily represented. It is therefore neither necessary nor advisable to treat a considerable quantity of solution as if the entire course of basic analysis were to be carried out. A small portion of the solution, say 5 c.c., may be tested with a drop of hydrochloric acid, and, failing a precipitate, with hydrogen sulphide. If a precipitate results, a larger portion of the solution may be analyzed. (See note 5.) Similarly, a small portion of the filtrate from a group precipitation may be tested for the subsequent group.

The presence of a group or sub-group may in the majority of cases be shown by adding a slight excess of sodic carbonate, boiling to expel carbon dioxide, and setting aside, if necessary, to allow precipitate to form. This does not of course apply to As, Na, K, Li, or to Mg or Zn if ammonium salts are present, nor is it reliable with some others in presence of ammonium salts.

Never use all of any solution for an analysis or for a test. Use as much as will ensure good results, and reserve a portion in case repetition of the analysis is necessary.

Apply as many confirmatory tests as are necessary for complete identification. (At least 10 c.c. of the original solution are to be saved until the report is examined.)

(1) **Bi** (also **Sb**) is occasionally precipitated as basic chloride with hydrochloric acid, but dissolves in excess. Compare N., p. 17, note 5.

(2) **If the solution is alkaline**, many substances may be precipitated by acidification. See H., p. 35, foot-note; N., p. 17, note 6.

(3) **Test for Pb in solution of chloride.** In case sulphuric acid causes a precipitate, it is well, after washing by decantation, to test this with hydrogen sulphide to be certain that it was not due to presence of a soluble Ba salt left by incomplete washing of the original precipitate from hydrochloric acid.

(4) **Precipitation of Sulphides.** Great care should be taken in the precipitation with hydrogen sulphide. Avoid excess of acid and

do not heat to *boiling*. Wait until the precipitate has settled and test for complete precipitation. Compare N., p. 18, notes 1-4.

(5) In case of **failure to get an immediate precipitate** with hydrogen sulphide, do not report absence of As unless a portion of the solution, saturated with hydrogen sulphide and corked for some hours, still gives no precipitate. Compare N., p. 18, note 6.

(6) P. 36, H., line 10, **read**: "It must be washed with hot water until the washwater no longer reacts acid."

(7) **Separation Group VI from Group V.** Transfer the precipitate to a test-tube and pour off excess of water used, so that residual volume containing suspended precipitate is about 10 c.c. Add 5 c.c. colorless ammoniac sulphide. If this does not effect complete solution, add 1 to 2 c.c. yellow ammoniac sulphide, warm *gently* and allow to stand 5-10 minutes.

The addition of hydrochloric acid to the filtrate (H., p. 37, par. 2) will show presence of Group VI. If Group VI is present, complete separation from Group V should be assured by treating residue again with small quantity of ammoniac sulphide mixture, filtering and testing with hydrochloric acid.

When Group VI has been separated, the residue should be well washed before treatment with nitric acid.

The presence or absence of Group VI may be judged by comparing the nature and amount of the precipitate caused by hydrochloric acid in the solution with that caused in the same amount of ammoniac sulphide mixture. Be sure of acidity. Compare N., p. 19, note 2.

The separation of Group VI from Group V should always be tried, as a **preliminary test**, with a portion of the precipitate if the latter is in sufficient quantity. The amount of reagents will of course be modified to suit the amount of precipitate taken.

The sulphides of Group VI have a strong tendency to assume the **colloidal condition**, and in this are difficult if not impossible to filter. Coagulation of the colloid solution is often accelerated by the addition of some electrolyte; for example, a few drops of baric chloride or aluminic sulphate.

(8) **Cupric sulphide** is somewhat soluble in yellow ammoniac sulphide, and if a small quantity is present it may be entirely dissolved. It is precipitated from ammoniac sulphide solution in a dirty brownish form. Hence if a test in the original solution with ammoniac hydroxide (which it is always well to make) shows Cu, an apparent precipitation of Group VI in the ammoniac sulphide solution may turn out to be not As, Sb, or Sn, but Cu.

(9) **Mercury** may be tested for by stannous chloride, provided the solution contains no oxidizing agent. Compare N., p. 21. Absence of lead must be assured.

Any residue from the treatment with dilute nitric acid should be tested for mercury, even though not black.

(10) P. 37, line 11, H. **Insert:** Confirm Bi by solution in a few drops concentrated hydrochloric acid, boiling down nearly to dryness in moving test-tube, and adding much water; white precipitate of bismuthous oxychloride. Compare N., p. 22, note 3.

(11) An alternative **Test** for **Bismuth** may be as follows: To a few drops of stannous chloride add just enough sodic hydroxide to re-dissolve the precipitate which forms at first. To this solution, which should be cold, add a few drops of the bismuth solution, which should not be strongly acid. If present, metallic bismuth, black, is precipitated.

(12) **Separation Cu from Cd**, line 17, p. 37, H. **Insert:** Filter the mixed sulphides, wash free from hydrogen sulphide, break hole in paper, and wash into test-tube with not over 15 c.c. water. If more, allow to settle, and pour off excess water. Add one-fourth the volume of dilute sulphuric acid and boil for a few minutes, closing test-tube with cork having Bunsen valve.

(13) A yellow precipitate with hydrochloric acid in the ammoniac carbonate solution should always be tested for **arsenic** in the bulb-tube (H., p. 38). The apparent deposit caused by the dry distillation of any organic matter that might be present should not be mistaken for arsenic, and any deposit should be tested by cutting the tube and gentle heating, on which the characteristic odor of arsenic may be recognized.

If the precipitate is so small that the bulb-tube test cannot be used, proceed as follows: Cut out the centre of the paper containing the precipitate and place it in a porcelain crucible. Add a crystal of potassic chlorate and a few drops concentrated hydrochloric acid. Warm until paper is destroyed, adding more acid if necessary. Expel chlorine, make just ammoniacal and filter the solution, which should consist of only a few drops, into a watch glass. Add a few drops more ammoniac hydroxide and a drop of magnesian sulphate. White, crystalline ammonio-magnesian arseniate is formed if As is present. Compare H., pp. 17, 47; N., pp. 24, 25, note 5.

(14) **Separation of Sb and Sn.** "The sulphides which have been freed from sulphide of arsenic by treatment with ammoniac car-

bonate, are, after washing, dissolved in not over 5 c.c. hydrochloric acid to which a *very* little potassic chlorate has been added." (Thus far as in H., p. 38, line 10.) Substitute now the following: The solution of antimonie and stannic chlorides diluted with three volumes of water is boiled to expel chlorine, then boiled for several minutes with half a dozen pieces of fine iron wire (card teeth). The test-tube may be set on iron gauze, over low flame. Sb is precipitated as a black soot-like deposit which separates easily from the iron. The stannic chloride is reduced to stannous. The solution must be colorless.

By rubbing the card teeth with stirring rod, separate the Sb from the iron as much as possible. Filter and transfer the Sb residue to the paper, removing the card teeth if they fall with the Sb into the paper. Test the filtrate for Sn with mercuric chloride.

The residue should always be confirmed for Sb, as follows: Wash thoroughly, dissolve in about 2 c.c. aqua regia, dilute with about 10 c.c. water, boil out excess of chlorine and add hydrogen sulphide. Orange Sb_2S_5 is precipitated, if Sb is present.

A black deposit on the iron, not readily detachable, may with care be tested as follows: Warm the washed iron with a few c.c. water containing a crystal of tartaric acid, about the size of a bean, and a drop of nitric acid. As soon as the deposit appears dissolved, pour off the solution, add a drop of hydrochloric acid and test with hydrogen sulphide. If much iron has not been dissolved the Sb may be recognized. Compare H., p. 38.

Groups III-IV.

(1) As the solutions given out for the special study of basic analysis contain only nitrates, chlorides, or sulphates, the possibility of the precipitation of an insoluble **phosphate** or **oxalate** by ammoniac hydroxide need not be considered in these solutions. But in the systematic course of analysis, where the solid has been dissolved in acid, the presence of phosphoric or oxalic acid must be considered before beginning the separation of Groups III-IV (H., pp. 40, 41; N., p. 38).

(2) It must be noted that the method given in *Hill* for the analysis of this as well as for other groups is of *general* application, and that it may be modified in special cases. In order to avoid unnecessary work, it is important to carry out the **preliminary tests**, N., p. 29, with due attention to notes 2 and 7 on page 30. If Al, Fe, and Cr

are all absent, it is evident that the baric carbonate treatment is unnecessary. If Al and a small amount of Fe are present and Cr absent, which can be ascertained by the fusion test, the baric carbonate treatment may still be omitted. (See N., p. 36, for method.) The preliminary test will give much information and may save much subsequent work.

If Mn is present in large quantity, it may be precipitated slowly by ammoniac hydroxide. Compare N., p. 31, note 11. The speed of precipitation will suggest its presence and the fusion test will confirm it.

(3) The **ammoniac sulphide** must not be more than slightly colored, and must give little more than a slight precipitate when acidified.

(4) A **dark residue** after treatment with cold, dilute hydrochloric acid, if not due to traces of cobaltous or nickelous sulphides, may be **sulphur** colored by occluded ferrous sulphide. The aqua regia solution, on adding ammoniac hydroxide and filtering, will show absence or presence of Co and Ni by test with ammoniac sulphide. Fe may be proved by dissolving the ammoniac hydroxide precipitate in dilute hydrochloric acid and adding potassic thiocyanate. Compare N., p. 32; notes 2-5, p. 33.

(5) If **Ni alone** is indicated by the borax bead, traces of Co may be looked for by the potassic nitrite method. (N., p. 33; p. 34, note 9.

(6) An excellent **test for Co** also is the following: The solution must be only slightly acid and must not contain nitrous acid. Add considerable ammoniac thiocyanate (end desk), then 5 to 10 c.c. of a mixture of amyl alcohol and ether (end desk). Close test-tube with thumb and shake. Allow to settle. A blue layer at top shows cobalt. If the layer is reddish (iron) add a few drops sodic carbonate and shake again. The layer should now be blue if cobalt is present, colorless if iron alone was present.

(7) The **General Remarks**, N., pp. 34-36, will assist in understanding what process is best followed subsequent to the separation of Co and Ni.

(8) After dissolving **hydroxides of Fe, Al, Cr**, and excess of baric carbonate in dilute hydrochloric acid, heat to boiling and filter if necessary.* If ammoniac hydroxide causes no precipitate in the solution, do not proceed further.

* It often happens that SO_4 ions are present at this point, hence baric sulphate is precipitated.

(9) **Aluminum.** Traces of silica find their way into the analysis from the glass of reagent or supply bottles, beakers, etc., and considerable quantities may occur in alkaline reagents, particularly sodic hydroxide and peroxide. The addition of ammoniac chloride to the sodic hydroxide solution may therefore precipitate silicic acid, $\text{SiO}(\text{OH})_2$, from the sodic silicate therein contained, either alone or in addition to the aluminic hydroxide which is thrown out by the action of ammoniac chloride on the sodic aluminate. It is also possible that the sodic hydroxide may contain traces of aluminate. It frequently happens, therefore, that the student mistakes a slight precipitate of silicic acid for aluminic hydroxide, or that the precipitate, whether Al alone or mixed with Si, may be due to these impurities in the reagents. To avoid this confusion as far as possible, the following rules should be observed: —

(a) Do not evaporate solutions in a glass vessel, nor boil in a glass vessel longer than necessary.

(b) If the substance is known to be a silicate, remove the silica carefully by the method given on page 53 before beginning the basic analysis.

(c) Make blank tests of the sodic hydroxide and peroxide with ammoniac chloride, or with hydrochloric acid and ammoniac hydroxide, using as nearly as possible the same amounts of the reagents as you have used in the analysis. If the blank test shows no precipitate similar to that which you have obtained, you are justified in reporting Al, provided there has been no chance for introduction of Si other than through the reagents tested.

(d) The precipitate itself may be tested, if in sufficient quantity. Filter through the smallest possible filter, wash the paper thoroughly (the precipitate may be too small to see), dry, and ignite on platinum foil. Fuse the residue, still on the foil, with a crystal of acid potassic sulphate. The silicic acid is insoluble; the aluminic hydroxide is changed to sulphate. Dissolve in 1 to 3 c.c. water, filter through smallest possible filter, add ammoniac hydroxide to filtrate. Al is precipitated as hydroxide, if present.

(e) Consult the assistant on all doubtful precipitations of Al.

(f) If the filtrate from Groups V–VI, free from hydrogen sulphide, phosphates and oxalates, etc., gives a white gelatinous precipitate with ammoniac chloride and ammoniac hydroxide, the chances

are in favor of its being Al. This precipitate may readily be tested for Al according to (d).

(10) A residue after oxidation with alkaline peroxide is of little importance as a **test for Fe**.

Iron need not be tested for in original solution if the alkaline peroxide treatment gives no residue in separation of Fe from Al and Cr. Care should be taken to distinguish small amounts of iron from unimportant traces, since the color tests are very delicate.

(11) A colorless solution contains no appreciable quantity of **chromic salt** or chromate. A white precipitate with plumbous acetate is *not* plumbous chromate and is due to too little acetic acid; more acid will usually dissolve.

(12) H., p. 40, 5th line from bottom: **read** $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ for BaCl_2 .

H., p. 40, 4th line from bottom: **read** PbCrO_4 for BaCrO_4 .

(13) The filtrate from baric carbonate precipitate may become turbid from separation of baric carbonate out of baric acid carbonate solution. Disregard.

(14) H., p. 41, line 14. **Omit** words "and boil."

(15) H., p. 41, line 16. For "wire" **read** "foil."

(16) A small precipitate, not evidently manganous hydroxide, should always be tested for **Mn** by fusion as directed. The color of the potassic manganate is characteristic, but a comparison test should be made with a bit of manganese peroxide. The presence of Fe and Cr can be readily ascertained in the fusion, if desired. Compare N., p. 37, note 3; p. 42, note 3.

(17) **Zincic sulphide** should settle after standing and appear more or less flocculent. It is also soluble in dilute hydrochloric acid. Sulphur does not dissolve in dilute hydrochloric acid, does not settle quickly, and remains finely divided. Compare also N., p. 38, note 2.

(18) If **phosphoric** or **oxalic** acid is present in the filtrate after separation of Co and Ni, the solution must first be tested for Ba(SrCa) before adding baric carbonate, and must be treated with sufficient ferric chloride to fix the acids as ferric phosphate and oxalate when the baric carbonate is added. H., pp. 41-42; N., pp. 38-43, bracketed portions.

Groups I-II.

(1) **The filtrate from Groups III-IV** should never be allowed to remain alkali for any length of time. Ammonic hydroxide absorbs carbon dioxide from the air, and the carbonate thus formed precipitates Ba, Sr, or Ca, which might be filtered off and lost. Compare N., p. 32, note 5. The filtrate, acidified with dilute acetic acid, should be immediately evaporated, filtered from separated sulphur or NiS, if any, and set aside for separation of Group II. Compare also foot-note, H., p. 39; N., note 3, p. 31. Care should also be taken not to allow the ammonic sulphide in the filtrate to become oxidized to sulphate, as Ba and Sr would be precipitated. Evidently, the reagent ammonic sulphide must contain no sulphate. Similarly, separated sulphur in Ba, Sr, or Ca solution must have no chance to become oxidized.

It is well to make a preliminary test for Ba (or Sr) in the original solution by adding dilute sulphuric acid. The spectroscope (H., p. 44) will show presence of Ba or Sr if the precipitate is filtered off. The precipitate may be shown to consist partly or entirely of lead sulphate by its action with hydrogen sulphide and its solubility in ammonic acetate. (H., p. 32; N., p. 76, note 2, c.)

(2) Never report absence of **Ba, Sr, or Ca** on failure to get precipitate with ammonic carbonate. There might be still traces or even small amounts which were not precipitated on account of excess of ammonic carbonate or chloride. Such an excess might also carry traces of Ba, Sr, and Ca into the filtrate, hence a slight precipitate with sodic phosphate should not be accepted as Mg unless absence of Ba, Sr, and Ca is proved. See foot-note, H., p. 43; N., note 2, p. 46.

(3) The treatment referred to in the last note may be made a **preferable treatment** for Groups I-II, as follows, provided the solution is dilute and free from any ion from which sulphur may be separated on addition of acid: Test a small portion of the group solution with dilute sulphuric acid. If a precipitate is formed from this or a larger portion, test in spectroscope for Ba and Sr, and examine the filtrate for Ca and Mg; or, to ascertain the relative amounts of Ba and Sr, proceed with the rest of the group solution according to the usual method. But if there is no precipitate with sulphuric acid, Ba and Sr are absent, and the rest of the solution may be treated as if Ca and Mg alone were present.

(4) In testing with calcic sulphate for presence of Ba or Sr, a small quantity of **Ba** may be **confounded** with a large quantity of **Sr**. If there is any doubt, test another small **portion** of the solution with potassic chromate. The amount of calcic sulphate added should not be less than 10 c.c.

(5) In case calcic sulphate gives **no precipitate** in the acetate solution after standing, the solution may be evaporated one-half in moving test-tube and allowed to stand longer. The evaporation must not of course be carried to the crystallizing point of the calcic sulphate solution.

(6) **Elimination of Ba.** Instead of precipitating with potassic chromate in the cold, precipitate hot, allow to settle and filter at once. The solution must be refiltered if not perfectly clear.

(7) A small amount of **Ca** requires time for complete precipitation as oxalate.

(8) Do not heat the residue containing Group I at a higher temperature than is necessary to drive off the ammonium salts. Ignition at a high temperature will volatilize the chlorides of Na, K, and Li.

(9) The separation of **magnesium** from Group I by means of baric hydroxide should be carried on in porcelain.

(10) Do not make flame or spectroscope tests unless there is a distinct **residue** on evaporation and ignition, *i. e.*, do not report Group I unless you can distinctly see a residue. If there is not a definite residue, add a few drops of water, filter through a very small paper into a watch glass and allow to evaporate spontaneously. A slight film on the watch glass, without crystals, may be disregarded.

(11) The **test for K** with chlorplatinic acid may be made if absence of NH_4 salts is assured by thorough ignition. A trace of ammoniac chloride left in the Group I residue would vitiate the test. Compare notes 2, 5, pp. 48-49, N.

If a solution to be tested for potassium contains iodine ions, these must be removed by evaporation with hydrochloric acid, since chlorplatinic acid is reduced by an alkaline iodide to chlorplatinous acid with separation of iodine.

ACID ANALYSIS.

Pages 45-53, H.; pp. 50-64, N.

The acids are not separated after precipitation by general reagents, as in basic analysis. A general reagent, in acid analysis, shows the presence or absence of the group, but does not separate one group from another.

The general reactions of acids are first taken up (H., pp. 15-25). The reactions which are of especial qualitative importance are indicated below, and are to be carefully studied. Mark the corresponding paragraph in Hill. Take brief notes on the sheets provided and write the equation for the reaction in its proper place.

PRELIMINARY WORK ON THE PROPERTIES OF ACIDS.

Group I, 1. (H., pp. 16-18.)

Sources: Potassic chromate (reagent); sodic arsenite and arseniate; sodic sulphite and thiosulphate, dissolved in water. See paragraph, *Concentration and Volume of Solutions*, page 8.

Chromates. To neutral potassic chromate add argentic nitrate (R); divide into two parts; add to one nitric acid, to the other ammoniac hydroxide.

To neutral potassic chromate add dilute sulphuric acid in excess (R), warm, add hydrogen sulphide in excess (R). Filter, expel hydrogen sulphide and precipitate with ammoniac hydroxide (R).

To neutral potassic chromate add dilute sulphuric acid, warm, and add sulphurous acid until color changes to that of chromic salt (R). Expel sulphur dioxide, precipitate by ammoniac hydroxide.

Arsenites. To neutral sodic arsenite add argentic nitrate (R); divide into two parts; to one add nitric acid, to the other ammoniac hydroxide.

To sodic arsenite add few drops dilute solution cupric sulphate, then sodic hydroxide to dissolve. Warm to bring about reduction of cupric hydroxide to cuprous (R).

Arseniates. To neutral sodic arseniate add argentic nitrate (R); divide into two parts; to one add nitric acid, to the other ammoniac hydroxide.

To sodic arseniate add ammonic chloride, ammonic hydroxide, and magnesic sulphate (R). Compare the similar reaction under Phosphates.

To 2 c.c. ammonic molybdate add drop or two of sodic arseniate acidified with nitric acid. Warm. Compare the similar reaction under Phosphates.

To acidified sodic arseniate add same volume hydrogen sulphide, cork, and allow to stand (R).

To acidified sodic arseniate add sulphurous acid, and boil (R). Expel sulphur dioxide, precipitate with hydrogen sulphide (R).

Sulphites. To solid sodic sulphite in two test-tubes add dilute hydrochloric acid (R), cap one test-tube with filter paper having drop of mercurous nitrate in centre (R); the other with a filter paper on which is a drop of acidified potassic iodate solution, to which starch solution has been added (R).

To hot sodic sulphite solution add baric chloride (R); add excess dilute hydrochloric acid, filter from sulphate, add bromine water to filtrate (R).

To sulphurous acid add hydrogen sulphide, allow to stand (R).

To sulphurous acid add zinc and hydrochloric acid (R), cap with filter paper having drop of plumbous acetate in centre.

Thiosulphates. To rather concentrated solution of sodic thiosulphate add dilute hydrochloric acid (R). Cap with paper having drop of mercurous nitrate, or drop of iodic acid and starch.

To dilute sodic thiosulphate add argentic nitrate until precipitate (R) no longer dissolves. Warm (R).

Group I, 2. (H., pp. 18-22.)

Sources: Sodic phosphate and ammonic oxalate (reagents); sodic fluoride and sodic silicate; borax and Rochelle salt, dissolved in water. See paragraph, *Concentration and Volume of Solutions*, page 8.

Phosphates. To sodic phosphate add argentic nitrate (R); divide into two parts; to one add nitric acid, to the other ammonic hydroxide.

To sodic phosphate add ammonic chloride, ammonic hydroxide and magnesic sulphate (R). Compare the similar reaction under Arseniates.

To 2 c.c. ammonic molybdate add few drops sodic phosphate acidified with nitric acid. To 2 c.c. molybdate add few drops solu-

tion of calcic phosphate in nitric acid. Compare the similar reaction under Arseniates.

To sodic phosphate add baric chloride (R); dissolve in least possible amount hydrochloric acid (R), and re-precipitate by ammoniac hydroxide (R).

Borates. To borax solution add few drops concentrated hydrochloric acid (R). Borax must be concentrated — best saturated.

To borax solution add dilute hydrochloric acid in excess. Dip piece of fresh turmeric paper in solution, dry at 100°, observe color. Add drop of sodic carbonate, observe color. Compare these colors with those obtained by similar treatment of turmeric without borax.

To borax solution add baric chloride (R); dissolve in least possible amount hydrochloric acid, try to re-precipitate by ammoniac hydroxide.

Oxalates. Warm a pinch of manganese dioxide with dilute sulphuric acid until carbonates, if any, are decomposed and carbon dioxide is expelled. Add a crystal of oxalic acid (R). Pour gas into lime water (R).

To ammoniac oxalate solution add baric chloride (R), dissolve in least possible amount of hydrochloric acid, re-precipitate with ammoniac hydroxide. Compare the similar reaction under Phosphates.

To ammoniac oxalate solution add calcic chloride (R), then try to dissolve in acetic acid.

Fluorides. To a little concentrated sulphuric acid in a perfectly dry test-tube add a pinch of calcic fluoride mixed with equal amount of sand. Warm (R). Test gas with hanging drop of water (R).

To sodic fluoride solution add baric chloride (R), dissolve in least possible amount of dilute hydrochloric acid; try to re-precipitate with ammoniac hydroxide. Compare similar reaction under Phosphates.

To sodic fluoride solution add calcic chloride (R), then try to dissolve in acetic acid. Compare similar reaction under Oxalates.

Tartrates. To solution Rochelle salt add baric chloride (R), dissolve in least possible amount of dilute hydrochloric acid; try to re-precipitate with ammoniac hydroxide. Compare similar reaction under Phosphates.

To excess Rochelle salt solution add few drops calcic chloride (R). If no precipitate at once, add a few drops acetic acid, warm, and rub the test-tube with rod until crystals form. Wash these by decantation and dissolve in sodic hydroxide; warm (R).

To rather concentrated solution Rochelle salt add acetic acid (R). Crystallization of acid potassic tartrate may be slow.

Carbonates. To sodic carbonate add hydrochloric acid (R). Pour liberated gas into lime-water (R).

Silicates. To a few c.c. silicate solution add excess hydrochloric acid (R), evaporate to dryness on water-bath (R), add hydrochloric acid and water, filter. Compare p. 53, note 2.

Sulphates. Sufficiently studied.

Group II. (H., pp. 22-24.)

Sources: Potassic ferrocyanide (reagent); sodic chloride, potassic bromide, potassic iodide, potassic cyanide, potassic ferricyanide, dissolved in water. See paragraph, *Concentration and Volume of Solutions*, page 8.

Chlorides. To concentrated sulphuric acid in perfectly dry test-tube add small amount mixture (well ground) of sodic chloride and potassic dichromate (R). Close tube by well-fitting cork carrying J-tube. Warm, and pass gas into water, having long arm of J-tube just at surface of water (R). Add to distillate few drops ammoniac hydroxide (R), then acidify with acetic acid (R) and add plumbous acetate (R).

el H. 207 **Bromides.** To very dilute potassic bromide add chlorine water (R). Add a little carbon disulphide, and shake.

Iodides. To very dilute potassic iodide add chlorine water (R). Add a little carbon disulphide, and shake.

To a very dilute potassic iodide solution add a few drops starch solution, then chlorine water.

Chlorides, Bromides, Iodides. To three test-tubes containing respectively sodic chloride, bromide, and iodide add few drops argentic nitrate, then dilute nitric acid (R). Try to dissolve in ammoniac hydroxide. Filter and acidify filtrate.

To small crystal chloride, bromide and iodide, each in separate tube, add concentrated sulphuric acid, and warm gently (R).

To mixture of *very* dilute bromide and iodide (in presence of carbon disulphide) add chlorine water, drop by drop, until iodine color disappears, then more chlorine until bromine disappears.

Cyanides. To dilute potassic cyanide add argentic nitrate, drop by drop (R), until precipitate is permanent (R). Divide into two parts; to one add nitric acid, to the other ammoniac hydroxide.

To dilute cyanide solution add drop of ferrous sulphate solution, then drop ferric chloride, then sodic hydroxide, and acidify with hydrochloric acid (R).

To cyanide solution in smallest beaker, add hydrochloric acid, cover beaker with watch glass having drop of yellow ammonic sulphide on under side (R). Allow to stand a few minutes, then rinse watch glass with few drops water into small test-tube, warm until sulphide is decomposed and solution is colorless, then add ferric chloride (R).

Handle cyanide carefully, and avoid inhaling from acid solution of HCN!

Sulphides. To drop of hydrogen sulphide diluted with a little water, add drop of argentic nitrate (R); divide, try solution in nitric acid and in ammonic hydroxide.

Ferrocyanides. To dilute ferrocyanide solution add argentic nitrate (R); divide, try solution in nitric acid and in ammonic hydroxide.

Ferric and cupric ferrocyanides have been studied.

Ferricyanides. To dilute ferricyanide solution add argentic nitrate (R); divide, try solution in nitric acid and in ammonic hydroxide.

Ferrous ferricyanide has been studied. To dilute ferricyanide solution add ferric chloride (R). Moisten paper with this solution and expose to light (R). To solution add sulphurous acid (R).

Group III. (H., pp. 24-25.)

Sources: Sodic acetate, potassic nitrate and chlorate, dissolved in water; see paragraph, *Concentration and Volume of Solutions*, page 8.

Nitrates. In rather strong solution of nitrate place bit of copper and add concentrated sulphuric acid (R).

To cooled concentrated solution of green ferrous sulphate add a few drops of the nitrate solution, incline test-tube and pour concentrated sulphuric acid slowly down the tube. Count 20 slowly and bring tube to upright position (R). There should be between sharply defined layers of ferrous sulphate and acid.

Chlorates. Action of concentrated hydrochloric acid on chlorates has been studied (R).

To a little sulphuric acid in small test-tube add a small crystal potassic chlorate (R) and set aside in rack. On no account heat.

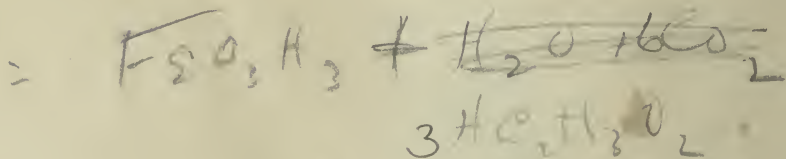
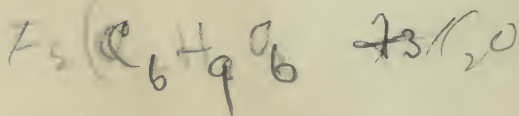
Handwritten notes:
 49200 + 3H4F...
 F...
 112100

Acetates. To sodic acetate crystals in test-tube add concentrated sulphuric acid (R). Odor.

To perfectly neutral solution of acetate add few drops ferric chloride (R). Warm until solution is colorless (R).

PROBLEMS IN QUALITATIVE ANALYSIS; UNKNOWN SUBSTANCES.

After the preliminary study of the acids the systematic analysis of some forty solid substances is taken up, comprising the main work of the second term. The directions for this work will be found under the head of "Systematic Course of Analysis," page 44, below.



*ADDITIONS AND CORRECTIONS IN GENERAL METHODS
OF ACID ANALYSIS.*

Group I. (H., pp. 46-50; N., pp. 55-58.)

Arseniates and Phosphates. Unless the test with hydrogen sulphide is carefully made (p. 23 [5]) the arseniate is liable to be reported as phosphate. The arseniate must be entirely reduced and the arsenic removed before the phosphate is tested for.

Sulphites in Presence of Thiosulphates. To 5 c.c. normal zinc sulphate add a few drops N/10 sodic nitroprusside, and then add the solution to be tested, previously neutralized exactly with acetic acid or sodic carbonate. A pink color appears in presence of sulphites, not in presence of thiosulphates. If the reaction does not appear at once, add a few drops potassic ferrocyanide.

Phosphates. The test depending upon the formation of ammonio-magnesium phosphate is applied only to a salt soluble in water.

Borates. The color imparted by boric acid to turmeric must not be confounded with that imparted by concentrated hydrochloric acid.

Oxalates. An insoluble oxalate may sometimes be conveniently decomposed by boiling with sodic carbonate solution. The filtrate after acidification and expulsion of carbon dioxide may be tested for oxalate. H., p. 49.

Oxalates in Presence of Carbonates. Expel carbonic acid by heating, after addition of the acid most suitable for the subsequent test for oxalate.

Oxalates in Presence of Fluorides. If fluoride has been found, test for oxalate with manganese dioxide and sulphuric acid. Try the solubility in acetic acid of the lime-water precipitate.

Fluorides. If the substance is decomposable by sulphuric acid and there is much of it, the addition of sulphuric acid in a test-tube and the test with hanging drop of water is sufficient. For small amounts the etching test must be applied and silica must be absent.

Tartrates. As all organic matter and salts of organic acids char when heated, the presence of a tartrate ought properly to be confirmed by the formation of calcic tartrate, soluble in cold sodic hydroxide, re-precipitated on boiling; and by the formation of acid potassic tartrate. Compare N., pp. 63-64.

Carbonates. The ordinary test with calcic hydroxide usually suffices. If small amounts of carbon dioxide are apparently given off on acidification, they may be detected by using a J-tube and baric hydroxide, boiling out air before adding acid and carefully protecting the baric hydroxide from the air.

Silicates. Detection is usually easy in preliminary examination. The separation is more important than the detection, and should always be complete before testing for other acids. See page 54, note 2.

Sulphates. The blowpipe test given in H., p. 50, is occasionally applicable in the case of insoluble substances.

Group II. (H., pp. 50-52; N., pp. 58-61.)

Chlorides. If bromides, iodides, and the cyanogen acids are proved absent, a precipitate with argentic nitrate, soluble in ammoniac hydroxide, is sufficient indication of chloride. In the majority of cases the slight turbidity which may ensue on addition of argentic nitrate can be ascribed to a trace of chloride.

Mixture of Halogens. If two or more halogens occur together, the detection of each requires some care.

Chloride and Bromide. Bromine has been proved present. Chlorine may be tested for by the distillation with potassic dichromate and sulphuric acid. Bromine also passes over, but is changed to bromate on heating the alkaline distillate, and does not interfere with the test. Compare N., pp. 60-61.

Chloride and Iodide. Iodine has been proved present. If only in small quantity, it does not interfere with the distillation test for chloride. But if in more than small quantity the original substance is fused with potassic dichromate in porcelain crucible or test-tube, until the iodine is expelled. The residue may then be distilled with sulphuric acid. Compare N., pp. 60-61.

Chloride, Bromide, Iodide. Bromine and iodine are proved present. The original substance is then fused with potassic dichromate and the residue distilled with sulphuric acid. Compare N., pp. 60-61.

The original precipitate with argentic nitrate may be digested with ammoniac hydroxide and the filtrate acidified with nitric acid. A precipitate shows chloride or bromide,—the color may assist in the conclusion; if bromide has been proved absent, the precipitate is due to chloride.

Bromide, Iodide. The chlorine water must be fresh and strong, the solution very dilute and acid, and the carbon disulphide freshly distilled. Compare N., p. 60.

Cyanides. If in considerable quantity the presence of cyanogen will have been recognized in the preliminary examination or basic analysis. Whether it is present as cyanide, ferro- or ferricyanide, or whether these are only present in small quantity, is now to be determined. A cyanide, treated *in the cold* with dilute acid, gives off hydrocyanic acid; ferro- and ferricyanides on heating. The presence of hydrocyanic acid may be recognized by the test with yellow ammonic sulphide (see page 35).

Ferro- and Ferricyanides. Insoluble ferro- and ferricyanides are boiled with dilute sodic hydroxide, filtered, and the acidified filtrate tested. Compare H., p. 52. Owing to the ease with which an alkaline ferricyanide is reduced in solution, it is often difficult to determine with certainty the presence of a small amount of insoluble ferricyanide, since, after boiling with sodic hydroxide, the filtrate may contain sodic ferrocyanide.

Sulphides. If dilute hydrochloric acid alone produces no hydrogen sulphide, add a bit of zinc. Compare N., p. 60. The possibility of the presence of As, hence formation of arsine, must not be forgotten, hence the tube should be placed under the hood.

Usually, in getting a sulphide into solution, its presence is evident from the separation of sulphur and the formation of sulphuric acid (by oxidation) in the acid solution.

Nitrites. If in quantity, the solution on acidification gives off nitrogen peroxide. The acid solution liberates iodine from potassic iodide, which may be recognized by starch.

Group III. (H., pp. 52-53; N., pp. 61-63.)

Nitrates. The ferrous sulphate should be in the form of fresh green crystals. A drop of dilute sulphuric acid will often make the solution clear.

Nitrates in Presence of Interfering Acids.

Chlorates. Warm in a test-tube with dry sodic carbonate until a portion gives no test for chlorate. Then test for nitrate. Compare N., pp. 62-63. Or, add excess sodic hydroxide, boil to expel any ammonia which may be present, and reduce by boiling with zinc dust. The nitrate is converted to ammonia, recognized by odor or by

turmeric; the chlorate to chloride. Test a portion of the solution, after acidifying with nitric acid, with argentic nitrate. If the original solution contained chloride, this must obviously be removed, — by precipitation with argentic sulphate and filtration. This filtrate, in case excess of argentic sulphate is present, is, after boiling with sodic hydroxide, filtered from argentic oxide before reducing with zinc.

Nitrites. Distinguished by tests given under Group II. The acidified solution may be warmed until it ceases to give any test with potassic iodide and starch. Neutralize exactly and test for nitrate. Small amounts of nitrate in presence of nitrite cannot be detected with certainty, since nitrous acid is always partially changed to nitric acid in solution.

Chromates. The chromate may be precipitated by plumbous acetate and filtered off; or it may be reduced in acid solution with sulphurous acid, the chromium precipitated as chromic hydroxide and the filtrate tested for nitrate. Compare N., p. 63.

Iodides. Use a small quantity of substance, dissolve in a little water, acidify with dilute sulphuric acid, and add argentic sulphate, carefully, until complete precipitation. Filter, make slightly alkaline with sodic hydroxide, evaporate to a small bulk, filter into the ferrous sulphate solution, and proceed with the test. Compare N., p. 63.

Bromides. The presence of a small amount of bromide does not interfere. Large amounts should be removed as under iodides in the previous paragraph.

Chlorates. A nitrate when heated with concentrated hydrochloric acid might be mistaken for chlorate. Hence cover the substance with water before adding acid.

Acetates. The presence of acetic acid in more than small quantity is generally recognized in the preliminary examination and may be confirmed by formation of ethyl acetate (N., p. 63) or of the basic acetate of iron (H., p. 53). In small quantity, particularly in presence of other organic acids, the detection is difficult, but it is often advisable to distil the substance with dilute sulphuric acid and to evaporate the distillate, after exact neutralization, to a convenient bulk, which may be then tested for acetate.

GENERAL TESTS FOR ACIDS OF GROUP I, 2, AND II.

H., pp. 47, 48, 50; N., pp. 52, 53.

After the base or bases have been determined, consult Table of Solubilities (H., p. 55) and decide, from the nature of solvent used, what acids are absent.

Remove carbonate by adding *slight* excess of dilute hydrochloric acid (for Group I, 2) or dilute nitric acid (for Group II) and boiling off carbon dioxide.

Remove silicate by treatment with hydrochloric or nitric acid, evaporation to dryness, baking, taking up with dilute acid and filtration. See page 53, note 2.

Remove arsenites and arseniates by hydrogen sulphide in acid solution and filtering from sulphide of arsenic. Expel hydrogen sulphide from filtrate by boiling.

Remove sulphites by addition of slight excess of acid and boiling off sulphur dioxide.

Remove thiosulphates by addition of slight excess of acid, evaporation to expel sulphur dioxide and to coagulate sulphur, and filtration.

Chromates need not be removed, as their presence does not interfere with the group tests.

Excess of acid is to be avoided, as the subsequent formation of ammoniac chloride (Group I, 2) prevents precipitation by group reagents.

The general tests for Group I, 2, or II are not to be applied unless the above acids are absent or have been removed.

Occasions sometimes arise when bases must be removed before testing.

Group I, 2.

The solution must not be too dilute, nor too concentrated, and excess of ammonium salts must not be present. The tests fail also in some cases if much potassium or sodium chloride (or nitrate) is present.

The general tests are usually applied in aqueous solutions containing bases which form soluble salts with the majority of the acids of the group. It is obviously useless to make general tests in aqueous

solution when, from the nature of the base, but one or two acids *could* be present, and it is usually of no advantage to make general tests in an *acid* solution.

Procedure. Make slightly alkaline with ammoniac hydroxide.

A precipitate should not fall at this point if the last paragraph has been regarded. If the original solution was acid, and it is, nevertheless, desired to make general tests, the base should be removed if possible by the most suitable method, since the addition of ammoniac hydroxide may cause the combination with the base of all or the greater part of one or more of the acids. Compare N., p. 82. As the removal of bases by hydrogen sulphide may result in the formation of sulphate, by oxidation, the original solution may be tested for sulphate.

Divide into two parts. *a.* To the first add baric chloride. A precipitate indicates any or all of the group. Add dilute hydrochloric acid.

aa. *Complete solution* indicates absence of sulphate. Make just alkaline with ammoniac hydroxide. Re-precipitation shows phosphate or oxalate, unless the solution is unduly concentrated, when other barium salts would be precipitated.

ab. *A residue* indicates sulphate. Part of the precipitate may disappear, and the nature of the residue may be different, in which case the presence of other acids may be surmised.

[Boil to settle the baric sulphate, cool, filter, and make filtrate ammoniacal. Re-precipitation shows phosphates and oxalates, as above.]

It is evident that the procedure in the last paragraph is superfluous if the addition of calcic chloride (*b*) gives no precipitate.

No re-precipitation in *aa* or *ab* shows absence of phosphates and oxalates, unless large excess of ammoniac chloride is present.

b. To the second part of the ammoniacal solution add calcic chloride. A precipitate indicates any or all of group except sulphate, provided the solution is not concentrated. Add excess of acetic acid.

ba. *Complete solution* indicates absence of oxalate and fluoride.

bb. *Residue* indicates presence of oxalate or fluoride.

Make special tests for such of the group as are not distinctly shown to be absent or present by the general tests.

Owing to the solubility of baric and calcic metaborates in ammoniac chloride and other salts, a special test for borate must always be made.

Group II.

The solution is free from Group I, 1, carbonates and silicates, and is acid with nitric acid.

In case oxalate is present the amount of nitric acid must be considerable, otherwise argentic oxalate is precipitated.

Procedure. Add a very slight excess of argentic nitrate. A precipitate indicates any or all of the group.

The color and the action of direct or diffused light may suggest the presence of some member of the group.

Add ammoniac hydroxide in considerable excess, and digest for some time.

a. Complete solution indicates absence of iodides and ferrocyanides.

b. Residue indicates presence of iodides or ferrocyanides. Its nature may suggest identity. Part of the precipitate may have disappeared, and the presence of other acids may be surmised. Warm to settle the residue, filter, and acidify with nitric acid. A re-precipitation shows presence of other acids.

Make special tests for such of the group as are not distinctly shown to be present or absent by the general tests.

No general test is made for acids of Group III.

SYSTEMATIC COURSE OF ANALYSIS.

Systematic Qualitative Analysis is studied by the analysis of some forty substances, which constitutes a little more than a half-year's work.

The specimen tubes in which the substances are given out for analysis must be clean and dry. Remove the old and put on a fresh label, bearing desk number and series number of analysis (*e.g.* 56/1).

Note color, appearance, — particularly whether homogeneous or not. A magnifying glass is useful for this purpose.

Go through the preliminary examination carefully (H., pp. 25–30; N., pp. 65–71). Do not spend too much time *trying* to get results. Refer to “Additions and Corrections, Preliminary Examination,” p. 45, below.

Get the substance into solution or decompose it. (H., pp. 30–34; N., pp. 72–84.) Refer to “Additions and Corrections, Solution of Substance,” p. 49, below.

Make a basic analysis of the solution or solutions obtained.

Consult Table of Solubilities (H., p. 55) and decide from the nature of the base or bases and from solvent what group or parts of group of acids may be absent.

Make group tests for acids (p. 41, above) at least in the portion soluble in water, then special tests for such acids as might be present. Do not waste time testing for acids which, under the conditions, could not possibly be present.

Take brief notes in the Analysis Notebook according to the general suggestions below. Summarize bases and acids found, and state in what amount. Combine the bases and acids if possible, and make a report as to the salt or salts present from the data furnished by all your observations.

No report will be accepted based on preliminary work alone, nor without sufficient notes to show how the analysis was made.

SYSTEMATIC QUALITATIVE ANALYSIS. GENERAL SUGGESTIONS FOR NOTES.

Substance 1.

Feb. 11, 1901.

Light blue, crystalline. Larger lumps darker blue.

Prel. Ex. B. T. Water given off, neutral.

Sub. turns white.

Darkens at high temp., acid gas given off.

Ch. Metallic residue.

 $\text{Na}_2\text{CO}_3 + \text{Ch.}$ Reddish metallic residue. ? Cu.

Borax. O. F. blue.

I. F. reddish. ? Cu.

Fl. O.

 H_2SO_4 . Substance turns white.*Sol. in water* easily; reaction acid. 1 to 100 sol. made up.*Basic Anal.* HCl, H_2S —Black ppte. HNO_3 dissolves. H_2SO_4 O H_4NOH Dark blue sol. $\therefore$ Cu. H_2S , H_2SO_4 , H_2S OFilt. from Group V $(\text{H}_4\text{N})_2\text{S}$ O $(\text{H}_4\text{N})_2\text{CO}_3$ O Na_2HPO_4 O

No residue on evap.

Base is Cu.

Table of sol. May have parts of Group I, 2; II; III. Prelim. Ex. precludes more than traces of these, except SO_4 .*Acid Anal.* H_4NOH , BaCl_2 W. ppte, heavy.HCl does not dissolve $\therefore$ SO_4 AgNO_3 Faint turbidity, sol. H_4NOH . $\therefore$ Trace Cl?*Bases*

Cu.

Acids

Cl (trace)

 SO_4 Report: Cupric sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, containing trace chloride.ADDITIONS AND CORRECTIONS, PRELIMINARY
EXAMINATION.

A. Heating in Bulb-tube. (H., pp. 25–27; N., pp. 66–68.)
 Make tube carefully, according to model. Walls of tube must be clean and dry. Put only a small amount of substance into bulb. Heat first gently, then strongly. Test for gaseous products by smell, application of flame to mouth of tube, insertion of spark.

Some of the following changes *may* occur : —

1. *Water* may be driven off and deposited on walls. Test with test-papers.

2. *Gas* may be given off. Observe color, odor, inflammability, support of combustion.

3. All or a part of the substance may *sublime*. Observe color of *sublimate* and appearance under lens.

The following change *generally* occurs : —

4. A *residue* differing from the original substance is left. Observe color, hot and cold, appearance, action of drop of dilute acid.

The interpretation of such changes as may occur (H., pp. 25–27; compare N., pp. 66–68) becomes easier with practice. Beginners, having found a definite change or none at all, should pass quickly to —

B. Heating on Charcoal before the Blowpipe. (H., pp. 27–28; N., p. 68.) Scoop out a round hole in the charcoal with the end of the pincers, lay a little of the substance in the hole, and direct the *inner* flame of the blowpipe against it, at an angle of about thirty degrees.

Some of the following results *may* be noticed; for interpretation see H., pp. 27–28; N., p. 68 : —

1. The substance may *volatilize* completely.

2. It may melt and be *absorbed* by the charcoal.

3. The volatilized substance or oxidation products may *condense* on the charcoal in front of the flame in the form of a *coating*.

4. The substance may *deflagrate* when heated.

5. The volatile products may have an *odor*.

The following change most commonly takes place : —

6. A *residue* consisting of reduced, decomposed or unaltered substance is left, with or without coating.

a. If this residue is white, use cobaltous nitrate as directed.

Arseniates, if not reduced, and borates will give a blue color similar to phosphates.

b. If the residue is not white, and not obviously metallic, the reduction may be again tried in presence of a flux of sodic carbonate.

A yellow mass may indicate Cr; a blue-green mass, Mn.

C. Heating in a Borax Bead. (H., pp. 28-29; N., p. 69.) Make a loop in platinum wire about one-eighth inch diameter, and melt a bead in it, taking care that the bead is perfectly colorless and transparent. Take up a little of the substance on the cold bead, and heat carefully in the outer flame until entirely melted. Remove from the flame and note the changes of color, if any, while the bead is cooling. Then repeat the heating and observation in the inner flame.

Microcosmic salt is often used in place of borax, the resulting bead of sodic metaphosphate giving similar colors. It is particularly useful in detecting silica.

Unless the substance be finely powdered, the small portion picked up on the bead may be only one component of a mixture.

D. Heating in the Colorless Flame. (H., p. 29; N., pp. 70-71.) Ignite the platinum loop until there is absolutely no color imparted by it to the flame. Moisten a little of the substance with a drop of dilute hydrochloric acid, take it up on the clean loop, and introduce it into the lower part of the flame at the outer edge.

Observe the flame also through a piece or pieces of blue glass which have been shown by trial to be thick enough to cut off the yellow sodium flame.

It is advantageous at this point to examine the flame in the spectroscope. (See Basic Analysis, p. 8.)

It is best to have separate wires for flame and bead tests.

E. Heating with Concentrated Sulphuric Acid. (H., pp. 29-30; N., p. 70, pp. 53-54.) Put 3 or 4 c.c. concentrated sulphuric acid into a small, dry test-tube, and add a small quantity of the substance. Warm very gently at first. If there is no violent action (*chlorates*), the heat may be increased, but never to the boiling point of the sulphuric acid. If the bulb-tube or charcoal has shown chlorate, do not use the sulphuric acid test, as there is great danger in heating a chlorate with concentrated sulphuric acid.

Notice whether any gas is given off, and if so, note the odor, color, inflammability, and action on test papers. A blackening of the acid shows the presence of an *organic salt* or *organic matter*, and there may be in addition sulphur dioxide given off through reduction of the sulphuric acid.

The following reactions are common : —

<i>Nitrates,</i>	}	Red fumes of nitrogen tetroxide.
<i>Nitrites,</i>		
<i>Chlorides,</i>		Sharp acid fumes ; white fumes with drop of ammonia on rod held at mouth of tube. (This may be due to the ammonium salt of other volatile acids as well.)
<i>Fluorides,</i>		Sharp acid fumes ; etching of tube ; drop of water made turbid.
<i>Sulphides,</i>		Odor of hydrogen sulphide ; sometimes of sulphur dioxide.
<i>Carbonates,</i>		Drop of lime-water made turbid.
<i>Sulphites,</i>		Odor of sulphur dioxide, without blackening.
<i>Thiosulphates,</i>		Odor of sulphur dioxide, precipitate of sulphur.
<i>Oxalates,</i>	}	Carbon monoxide, burning with blue flame.
<i>Cyanides,</i>		
<i>Acetates,</i>		Odor of vinegar.
<i>Bromides,</i>		Bromine given off, also sulphur dioxide.
<i>Iodides,</i>		Iodine given off, also sulphur dioxide.
<i>Chlorates,</i>		Yellow chlorine tetroxide given off.

In the systematic course of qualitative analysis, the preliminary examination, while often affording positive indications, is intended chiefly as a means of assistance in applying the proper solvents to the substance, and in making the subsequent complete analysis. For certain purposes, as in mineralogical work, and with certain other amplifying tests, it becomes of the highest usefulness and its results may be, for the purposes of the inquiry, final.

The tests given here are to be found in most text-books under the head of “ Analysis in the Dry Way,” or “ Blowpipe Analysis.”

ADDITIONS AND CORRECTIONS, SOLUTION OF SUBSTANCE.

(H., pp. 30-34; N., pp. 72-84.)

A compound is either soluble in water, soluble in acids, or insoluble in both water and acids. In a mixture we may have compounds of all of these grades of solubility. Hence it is necessary to determine in any substance presented for analysis whether we can separate it into two or three parts according to these grades.

If at the end of an analysis, it is desired to confirm the presence of a particular ion or to effect a particular separation, the analyst will choose the solvent best suited to his purpose.

Treat about one gram of the substance with 15 to 20 c.c. cold water.

It is best to weigh out one gram of the first few substances, in order to be able subsequently to estimate the approximate amount needed.

I. WATER SOLUTION.

If the substance dissolves in the cold or on subsequent warming, make it up to about 100 c.c., and proceed with the basic and acid analysis.

Test the solution with papers and note its color.

II. ACID SOLUTION.

If the substance does not dissolve in water after boiling for some time, allow it to settle and pipette off a few drops of the liquid. Evaporate this (filtered if not clear) carefully on a watch glass at 100°. If sufficient time, allow to evaporate spontaneously, as the nature of the crystals formed may assist in the identification. If considerable not easily volatilized substance is in solution, platinum foil over the flame will answer.

1. If an *appreciable residue*, the main portion is filtered, the filtrate set aside for analysis (same as *I, Water Solution*, above) and the insoluble portion washed with hot water until the washings give no test on evaporation. Suspend in 15 to 20 c.c. water and proceed to II, 2.

Often a very slight residue is left, consisting of shreds of paper, woody fibre or other organic matter, sand or other mineral matter. The lens will assist in the identification and it is not usually necessary to analyze such a residue.

Sometimes a salt becomes hydrolyzed by treatment with water, with formation of basic salt, so that a slight or a considerable residue may result. In this case part of the acid may be found in the insoluble portion, part in the aqueous solution. The aqueous solution, if previously neutral, will now be acid.

2. If *insoluble in water* or when freed from soluble portion and suspended in water, add a few drops concentrated hydrochloric acid, or nitric in case the preliminary examination has shown a metal forming an insoluble chloride.

a. Solution may take place at once or on warming. Note any changes accompanying solution (H., p. 31; N., p. 73, notes 3, 4). Make up to 100 c.c. or to a smaller volume in case the amount of dissolved substance is small, and proceed with basic and acid analysis of this portion *separately*.

b. Solution may not be apparent or may be partial. Allow to settle, pour off from residue and set aside. If evaporation test shows something in solution, the latter may be combined with subsequent acid solution or solutions, if any.

Boil the residue with 5 c.c. concentrated hydrochloric (or nitric) acid.

ba. Complete solution may take place. Combine with the portion soluble in dilute acid, and with subsequent aqua regia solution, if any, and expel excess of acid by evaporation. Dilute and proceed with basic and acid analysis.

bb. Solution may not take place. Add 2 c.c. concentrated nitric acid and boil.

If solution occurs, evaporate excess of acid, dilute with water and proceed with basic and acid analysis.

If solution is not apparent, or is only partial, dilute with water, and allow to settle. If test shows solution, filter and combine the filtrate with the acid solutions above, evaporating excess of acid before proceeding with the analysis.

Certain silicates may gelatinize with strong acid. In this case the mass is to be treated as elsewhere described for the elimination of silica (p. 53, A, 2). The silica obtained may be proved free from other substances by hydrofluoric acid. A residue after treatment with hydrofluoric acid is subject to fusion.

III. INSOLUBLE PORTION.

If all or a part of the substance does not yield to acids, it must be decomposed and converted into other compounds capable of solution and subsequent analysis.

With the exception of mineral products, the salts insoluble in acids are few. See H., p. 32; N., p. 76, note 1. The presence of some of these will have been suggested by the preliminary examination.

Two general methods of decomposition may be used: boiling with strong alkali and fusion with a flux.

1. **Alkali Treatment.** Some substances (H., p. 33) yield to boiling with sodic hydroxide (reagent) or sodic carbonate (reagent). Dilute and filter. Examine the washed residue, after solution in hydrochloric or nitric acid, for bases; the filtrate, after neutralization, for acids, and, in case sodic hydroxide has been used, for Al, Zn, and Pb.

In case the washed residue does not dissolve in acid, dry and fuse.

2. **Fusion.** Two kinds of fluxes may be used: *alkaline*, such as sodic carbonate, to which an oxidizing or reducing agent (potassic nitrate or cyanide) may be added if desired; and *acid*, such as acid potassic sulphate. (N., p. 78, note 8.)

Fusion is the usual method of decomposition. The substance, when free or if freed from any portion soluble in water or acids, is dried and fused as explained on p. 33, H. (pp. 52-54, below). Previous to fusion, the absence of all substances deleterious to platinum must be assured by special tests, which at the same time *may* show the nature of part or all of the substance and render further decomposition unnecessary.

Special Tests before Fusion.

(H., pp. 32-33; N., pp. 76-77, note 2.)

1. Ignite in porcelain crucible to expel C and S if present.
2. Test for Ag haloids in a potassic cyanide extract and remove if present.

Reduce by zinc and sulphuric acid in order to find haloids combined with silver. Filter from silver and excess of zinc, precipitate zinc in filtrate with excess sodic carbonate and test for Cl, Br, I. If the distillation test for Cl is

used it must be made with the evaporated filtrate from the zinc carbonate, since argentic chloride is not decomposed by potassic dichromate and sulphuric acid.

3. Test for plumbous sulphate in an ammoniac acetate extract (acetic acid nearly neutralized by ammoniac hydroxide) and remove if present.

A residue left after treatment with water, acids, alkalis and the tests above would be likely to contain BaSO_4 , SrSO_4 (CaSO_4), CaF_2 ; ignited Al_2O_3 , Cr_2O_3 , Fe_3O_4 , SnO_2 ; SiO_2 and native silicates; mineral products other than silicates, partially or not at all decomposed by previous treatment.

FUSION.

A. **Alkaline Fusion.** The usual mixture employed is that of sodic and potassic carbonates (H. p. 33), to which potassic nitrate is usually, but not always, added. Not too much of the substance should be taken, and the mixture should not fill the crucible more than two-thirds full. Heat gently at first, then at full heat of bunsen; finally, if necessary, over blast-lamp.

The oxidizing flame only must touch the crucible. The hot crucible must never be set upon any but a clean porcelain surface, and the crucible should be handled only by clean tongs.

A small amount of substance is most conveniently fused on platinum foil held in the flame by tongs. The foil can be rolled and placed in a test-tube in which the fused mass may be disintegrated by boiling with a small amount of water.

Certain fusions (*e. g.*, reducible metallic oxides, sulphides, phosphates with organic matter) can be made in a porcelain crucible or cover or bit of broken porcelain, but Al, Si, and such bases as occur in glaze can not be tested for in the fused mass. (N., p. 77, note 5.)

After the fusion is perfectly clear, and gas evolution, if any, has ceased, place the crucible on a cold porcelain surface and immediately insert the hooked end of your platinum wire, holding it in until fixed. When cold the fused button may perhaps be withdrawn. If not, set the crucible on its side in a small beaker, half cover with water, and boil until the button is disintegrated, replacing the water as it evaporates.

The subsequent treatment depends on the nature of the substance. If sulphates of Ba, Sr or Ca were present, we clearly cannot treat the disintegrated button directly with acids. (N., p. 77, note 3; p. 78, note 6.)

TREATMENT OF THE FUSED MASS, AFTER DISINTEGRATION
WITH WATER.

1. IF SULPHATES ARE PRESENT (as indicated by test in a portion of the filtered solution) filter, wash carefully and analyze the *residue* and *filtrate* separately.

a. Residue. Treat with a small amount of dilute hydrochloric acid, evaporate to dryness, heat at a temperature a little above 100° , add water and a little hydrochloric acid and filter if necessary.

The *filtrate* is to be examined for bases.

A residue here may be due to silica or some of the original substance unchanged by the fusion. The lens may assist in concluding, or the residue may be treated with hydrofluoric acid (see N., p. 77, note 2, e). If unchanged substance is present it may be again fused with alkali or with acid potassic sulphate (see B, p. 54, below).

b. Filtrate. Acidify with hydrochloric acid, evaporate to dryness, bake on ring over plate, take up with water and hydrochloric acid and filter from silica if any. Test filtrate for Al and Cr, possibly for acids. H_2F_2 must have been tested for in original substance.

2. IF SULPHATES ARE NOT PRESENT, which is oftener the case, the following procedure is employed, being particularly applicable to silica and the natural silicates and hence more general:—Treat the disintegrated button with excess of hydrochloric acid, evaporate to dryness on the waterbath, bake for 15–30 minutes on ring over plate, moisten with hydrochloric acid, boil out with water and filter from residue (silica and unaltered substance). The filtrate is to be examined for bases (except Group I) and for such acids as could be present.

The residue is examined with lens. Presence of unaltered substance is further assured by treatment with hydrofluoric acid. (N., p. 77, note 2, e.)

Alkalies in Silicates. If the fused substance turns out to be a natural silicate, Na, K, or Li must be tested for by fusion with an alkaline earth.

a. Fuse with four parts baric hydroxide. Boil out the fused mass with water and filter. Precipitate the excess of barium in the hot filtrate by dilute sulphuric acid, evaporate the filtrate to dryness, expel excess sulphuric acid and test for Na, K, and Li.

b. See N., p. 79, for method of decomposition with calcic carbonate and ammoniac chloride.

B. Acid Fusion. If a portion of the substance cannot be disintegrated by alkaline fusion (Al_2O_3 , aluminates, chromite of Fe), heat with 5 parts acid potassic sulphate until quiet fusion, but not until fumes of acid cease. Boil out with water, filter from residue, and test filtrate for bases.

If the residue proves to be anything but silica, test for Cr by fusion with sodic carbonate and potassic nitrate. (Compare N., p. 78, note 8.)

TREATMENT OF METALS AND ALLOYS.

(H., p. 32.)

Take not over 0.2 g. unless a special test is to be made for a small amount of some particular constituent. If the substance is obviously a metal or alloy, no preliminary examination is necessary. Treat at once with a mixture of one part concentrated nitric acid and three parts water, and warm until the metal disappears. Evaporate nearly to dryness at 100° , and take up with water and a little nitric acid.

A white residue may be metastannic acid or oxides of Sb, and may contain traces of As. Filter.

Dissolve the washed residue in hydrochloric acid and potassic chlorate and test for Sb and Sn.

Analyze the filtrate for bases except those of Groups I–II–VI. As or P may be tested for by ammoniac molybdate. Compare N., pp. 79–81.

If the oxides of tin and antimony are evaporated to complete dryness, or when dry are kept at 100° for some time, they become difficult to dissolve. In this case, recourse may be had to the directions on p. 80, N.

BLANK TESTS.

The reagents furnished in this course are as pure as the nature of the work demands, and contain no impurities which are likely to mislead the student.

It is a rule, however, in qualitative analysis to use no reagents which contain ions for which one is searching, or if this is not

strictly possible, to ascertain by a *blank test* the intensity of the reactions given by the impurity. By using, then, in the regular test the same quantity of reagent as in the blank, one can often be sure that the reaction is not wholly due to impurity, or conversely, that the reaction is probably due to impurity. It is obvious that a correct estimate would only be possible by quantitative analysis.

It is not intended in this course that blank tests shall often be made. Practice will suggest to the student when they are necessary. It is well, however, to be sure of the condition of the more frequently used reagents at all times, *e.g.*, to be sure that the hydrochloric acid is free from sulphates and the nitric from chlorides; that the ammoniacal hydroxide contains no carbonates, etc.



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ORDER AND STRENGTH OF REAGENTS.

M.W.Ts

WORKING DESK.

Upper Row.

142	1. Sulphuric Acid	Conc.
136	2. Nitric Acid	Conc.
324	3. Hydrochloric Acid	Conc
169	4. Acetic Acid	2N
	5. Acid Sodie Phosphate	N
	6. Calcic Sulphate, sat. sol.	N/100, approx.
	7. Plumbous Acetate	N
	8. Argentic Nitrate	N/10

Lower Row.

96	12. Sulphuric Acid, dil.	2N
53	13. Nitric Acid, dil.	2N
40	14. Hydrochloric Acid, dil.	2N
111	15. Ammonic Hydroxide	2N
208	16. Ammonic Sulphide	2N
	17. Ammonic Carbonate	2N
	18. Ammonic Chloride	2N
	19. Sodie Hydroxide	2N
	20. Calcic Chloride	N
	21. Baric Chloride	N

END DESK.

	1. Ammonic Molybdate	N
124	2. Ammonic Oxalate	N/2
	3. Potassic Chromate	N
	4. Potassic Ferrocyanide	N
	5. Potassic Thiocyanate	N
106	6. Sodie Carbonate	2N
171	7. Baric Hydroxide, sat. sol.	N/10, approx.
197	8. Baric Carbonate, emuls.	N
74	9. Calcic Hydroxide, sat. sol.	N, 20, approx.
120	10. Magnesic Sulphate	N
	11. Cobaltous Nitrate	N
	12. Ferric Chloride	N
	13. Mercurous Nitrate	N
	14. Mercuric Chloride	N/2
	15. Chlorine Water	N/5, approx.
	16. Bromine Water	N, 2, approx.
	17. Sulphurous Acid	2N, approx.